

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 05-065450
(43)Date of publication of application : 19.03.1993

(51)Int.Cl. C09D127/06
C09D 5/00
C09D 5/08
C09D 5/08

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(54) VINYL CHLORIDE PLASTISOL COMPOSITION

(57)Abstract:

PURPOSE: To provide the subject composition public as a paint to be applied for rustproofing on the back surface of automotive floors, comprising a PVC resin, plasticizer, inorganic filler, adhesivity-imparting agent and ferric dimethyl dithiocarbamate.

CONSTITUTION: The objective composition comprising (A) a PVC resin (pref. 30-40wt.% of a vinyl chloride-vinyl acetate copolymer), (B) a plasticizer (pref. 25-45wt.% of a phthalic ester), (C) an inorganic filler (pref. 5-20wt.% of surface-treated calcium carbonate), (D) an adhesivity-imparting agent (e.g. epoxy resin, blocked isocyanate resin), and (E) pref. 0.5-3wt.% of ferric dimethyl dithiocarbamate.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]

[Claim 1] The vinyl chloride plastisol constituent which is a vinyl chloride plastisol constituent which comes to contain polyvinyl chloride resin, a plasticizer, and a minerals filler at least, and is characterized by containing an adhesion grant agent and the second iron of dimethyl dithiocarbamic acid further.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the coating used for **** of an automobile etc. as an object for rust proofing, i.e., the vinyl chloride plastisol constituent suitably used as an under coat.

[0002]

[Description of the Prior Art] In recent years, extension of the life of an automobile and the technique of painting a vinyl chloride plastisol system under coat or a chipping-proof coating for example, with airless spray equipment to **** of an automobile, a side seal, a fuel tank, a front apron, a tire house, etc. are further known by improvement in a rust-proofing nature demand level etc.

[0003] The chipping-proof engine performance means the engine performance which controls the breadth of rust when breakage and this blemish of automobile sheathing produced by flying the pebble in the road surface under automobile transit, ballast, etc., and colliding with a car body (chipping) result in a substrate.

[0004] Since the chipping-proof engine performance was conventionally insufficient for the well-known vinyl chloride plastisol (PVC sol), these people etc. applied about the paint film piece by the intense chipping, and the PVC sol constituent which gave the resistance force to exfoliation by containing the adhesion grant agent for raising the adhesion reinforcement of a paint film while raising the paint film reinforcement of a PVC sol previously.

[0005] However, said constituent has a poor adhesive property to the second coat painted surface and the finishing painted surface which used various kinds of adherends, especially solid system coatings, and an acrylic metallic system coating.

[0006] Therefore, spreading of a up to [an electrodeposited paint film] is indispensable, and the paint line which can apply this constituent was limited.

[0007]

[Problem(s) to be Solved by the Invention] This invention was invented as a result of repeating research wholeheartedly, in order to cancel the trouble of the above-mentioned conventional technique, and it aims at offering the vinyl chloride plastisol constituent excellent in the adhesive property over various kinds of adherends especially the second coat painted surface, and the finishing painted surface.

[0008]

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, this invention is a vinyl chloride plastisol constituent which comes to contain polyvinyl chloride resin, a plasticizer, and a minerals filler at least, and contains an adhesion grant agent and the second iron of dimethyl dithiocarbamic acid further.

[0009] especially although it will not be limited especially if it is vinyl chloride resin currently used for the PVC sol, in order to acquire the paint film physical properties of high intensity conventionally as polyvinyl chloride resin which is the main constituent of this invention -- a vinyl chloride vinyl acetate copolymer -- all constituent weight -- receiving -- 25 - 45wt% -- desirable -- 30 - 40wt% -- it is used. If this amount used exceeds 45wt(s)%, workability, especially spray nature will worsen by viscosity and viscous increment. If this amount used is not filled to 25wt(s)%,

ordinary temperature and the chipping-proof nature in the time of proof against the cold will fall. [0010] 1500-2100 are suitable for the polymerization degree of the above-mentioned vinyl chloride vinyl acetate copolymer, and 1700-2000 are still more suitable for it. When a degree of polymerization exceeds 2100, a heat hardening property worsens, paint film reinforcement is insufficient, and chipping-proof nature is inferior. If a degree of polymerization does not fulfill 1500, since high paint film reinforcement is not obtained, chipping-proof nature will be inferior.

[0011] Moreover, 4.0 - 10.0% of the content of the above-mentioned vinyl acetate resin is suitable, and is still more suitable. [further 7.0 - 9.0% of] If a content exceeds 10.0%, a viscosity change with the passage of time will become large, and will spoil workability. If a content is not filled to 4.0%, a heat hardening property is bad and chipping-proof nature is inferior.

[0012] although there are phthalic ester, a dibasic acid ester, phosphoric ester, trimellitic acid ester, polyester, etc. as a plasticizer -- desirable -- phthalic ester -- all constituent weight -- receiving -- 25 - 45wt% -- it is used. When this amount used exceeds 45wt(s)%, a paint film becomes soft too much and chipping-proof nature is inferior. If the amount used is not filled to 25wt(s)%, the chipping-proof nature at the time of proof against the cold is inferior.

[0013] Although phthalic ester can also be used independently, an aliphatic series dibasic acid ester can also be used together in 0 - 15wt% as a secondary plasticizer. Although adipate is desirable as this aliphatic series dibasic acid ester, succinate, azelate, sebacic-acid ester, tetrahydrophthalic acid ester, etc. can also be used.

[0014] You may add independently, and it may mix mutually and these aliphatic series dibasic acid esters may be added. If the amount of the aliphatic series dibasic acid ester used exceeds 15wt(s)%, a heat hardening property will worsen and high chipping-proof nature will not be obtained. Moreover, since there is also a component which volatilizes with the heat at the time of heat hardening, problems, such as meat, and **, yellowing, arise.

[0015] In addition, when using together an aliphatic series dibasic acid ester, considering as 25 - 45wt% is suitable for the grand total of the amount of phthalic ester and the aliphatic series dibasic acid ester used.

[0016] a minerals filler -- all constituent weight -- receiving -- 5 - 20wt% -- it is used. If this amount used exceeds 20wt(s)%, lowering of workability, especially spray nature, lowering of chipping-proof nature, etc. generate and are not desirable. If it does not fill to 5wt(s)%, workability especially spray nature, and lappet nature will get worse.

[0017] Generally, as a minerals filler, although a surface treatment calcium carbonate, whiting, talc, clay, etc. are known, using a surface treatment calcium carbonate can also blend and use other minerals bulking agents for a surface treatment calcium carbonate most preferably.

[0018] As an adhesion grant agent, although an epoxy resin, acrylic resin, phenol resin, polyamide resin, blocked isocyanate resin, etc. can be raised, it is usable in that all are independent or combination.

[0019] Among these, the activity of blocked isocyanate is desirable. this amount used -- all constituent weight -- receiving -- 1.0 - 10.0wt% -- it is 2.5 - 8.0wt% preferably. When the amount used is less than [1.0wt%], the adhesive property of a paint film falls remarkably. 10. If 0wt% is exceeded, workability, especially spray nature will get worse.

[0020] Furthermore, as an indispensable component, the second iron of dimethyl dithiocarbamic acid is added. the second iron of dimethyl dithiocarbamic acid -- all constituent weight -- receiving -- 0.5 - 3wt% -- it is used.

[0021] Unless the amount used reaches to 0.5wt(s)%, effectiveness of this invention cannot be attained, and although the effectiveness of this invention can be attained if 3wt(s)% is exceeded, it becomes disadvantageous in cost. Effectiveness of this invention cannot be attained in any dimethyldithiocarbamate other than the second iron of dimethyl dithiocarbamic acid.

[0022] It is possible to add the component of the following arbitration in the vinyl chloride plastisol constituent of this invention if needed in addition to the above-mentioned indispensable component.

[0023] What is necessary is just to add organic and/or inorganic balun, in order to attain lightweightization of the vinyl chloride plastisol constituent of this invention.

[0024] as for example, organic balun -- hollow resin powder -- all coating weight -- receiving -- 0.3 - 4.0wt% -- desirable -- 0.4 - 3.0wt% -- it is used. As this hollow resin powder, although there are

amino resin, phenol resin, polyester resin, polyolefin resin, acrylonitrile resin, silicone resin, vinylidene-chloride acrylonitrile copolymerization resin, etc., vinylidene-chloride acrylonitrile copolymerization resin is desirable in respect of especially lightweight-ized effectiveness and thermal resistance.

[0025] If this amount used exceeds 4.0wt(s)%, paint film reinforcement will be insufficient and chipping-proof nature will be spoiled. Unless it fills the amount used to 0.3wt(s)%, specific gravity does not fall and it does not contribute to lightweight-ization.

[0026] Moreover, the front face of hollow resin powder can also use the hollow-like filler by which coating was carried out with talc, titanium oxide, a calcium carbonate, etc. Addition wt% in this case is the amount converted into the weight of a resinous principle.

[0027] The particle size of the hollow resin powder used for this invention is 200 micrometers or less, and is 80 micrometers or less preferably. Since the variation in pattern width of face arises in the case of an activity, and gun plugging etc. will arise when applying with airless spray further if particle size exceeds 200 micrometers, it is not desirable. In addition, that engine performance of the particle size of this hollow resin powder is so good that it is fine.

[0028] Moreover, glass balun etc. can be used as inorganic balun.

[0029] As a stabilizer, lead salt, metallic soap, an organotin compound, etc. can be used.

[0030] Titanium oxide, carbon black, etc. can be used as a coloring agent.

[0031] As a desiccant, they are CaO, aluminum 2O₃, and CaCl₂. It adds.

[0032] As a CHIKUSO agent, water silicic acid, a silicic anhydride, organic bentonite, etc. may be added.

[0033] As a viscosity controlling agent, various solvents, for example, a paraffin series solvent, a naphthene solvent, an aroma tick solvent, etc. can be used.

[0034] In addition, additives usually used for the vinyl chloride plastisol constituent, such as a thickener and an antifoaming agent, can also be added further.

[0035] What is necessary is to distribute said polyvinyl chloride resin in a plasticizer, and just to perform a bulking agent, an adhesion grant agent, etc. by well-known approaches, such as initial-complement-adding and mixing, continuously, in order to prepare the vinyl chloride plastisol constituent of this invention.

[0036] In order to use the vinyl chloride plastisol constituent of this invention, it can carry out by spraying with well-known airless spray etc., or applying by a brush etc. Although it can choose according to a request, if there are about 300-800 micrometers of this spreading thickness, it is enough.

[0037]

[Effect of the Invention] As stated above, since adhesive strength comparatively sufficient also by low-temperature printing is obtained while excelling in the adhesive property over the second coat painted surface and the finishing painted surface, the vinyl chloride plastisol constituent of this invention is very suitable as well as various adherends and especially the electrodeposited painted surface as an under coat which can respond to various paint line configurations and is used for **** of an automobile etc. as an object for rust proofing.

[0038]

[Example] The example of this invention is given and explained below.

[0039] Mixed distribution of the second iron of dimethyl dithiocarbamic acid 1.0wt% was carried out calcium oxide 2.0wt% surface-preparation calcium-carbonate 15.7wt% phthalic ester 33.3wt% using the kneader mixer blocked isocyanate (alkylphenol blocked isocyanate, NCO(%) = 3.2%) 8.0wt% example 1 vinyl-chloride-vinyl-acetate-copolymer (degree-of-polymerization 1900, 8.0% of vinyl acetate contents) 40wt%.

[0040] subsequently, below the bottom of reduced pressure (80MMHg) -- degassing -- stirring processing was carried out, the filter (60 meshes of elements) was used and filtered, and the constituent was prepared. Using the obtained constituent, various kinds of performance tests were performed and the result was shown in a table 1.

[0041] As well as the electrodeposited painted surface, the adhesive property over the second coat painted surface and the finishing painted surface was excellent, spreading workability is good, and is equipped with outstanding rust-proofing nature and endurance, and the obtained constituent has

checked that it was very suitable as an under coat used for **** of an automobile etc. as an object for rust proofing so that clearly from the test result of a table 1.

[0042] Example 2 vinyl-chloride-vinyl-acetate-copolymer (degree-of-polymerization 1900, 8.0% of vinyl acetate contents) 40wt%, Phthalic ester 33.3wt% and surface treatment calcium-carbonate 15.7wt%, calcium oxide 2.0wt% and blocked isocyanate (alkylphenol blocked isocyanate --) NCO (%) = 3.2%wt[4.0] %, an epoxy resin (a bisphenol A type) Weight per epoxy equivalent: 950 3.8wt%, latency curing agent (dicyandiamide) 0.2wt%, second iron of dimethyl dithiocarbamic acid 1.0wt% was processed like the example 1, and the constituent was prepared. Using the obtained constituent, various kinds of performance tests were performed and the result was shown in a table 1.

[0043] As well as the electrodeposited painted surface, the adhesive property over the second coat painted surface and the finishing painted surface was excellent, spreading workability is good, and is equipped with outstanding rust-proofing nature and endurance, and the obtained constituent has checked that it was very suitable as an under coat used for **** of an automobile etc. as an object for rust proofing so that clearly from the test result of a table 1.

[0044] Example 3 vinyl-chloride-vinyl-acetate-copolymer (degree-of-polymerization 1900, 8.0% of vinyl acetate contents) 40wt%, Phthalic ester 33.3wt% and surface treatment calcium-carbonate 15.1wt%, calcium oxide 2.0wt% and resin balun (hollow resin powder (vinylidene-chloride acrylonitrile copolymerization resin --)) Matsumoto Yushi-Seiyaku trade name microsphere F-80 0.6wt%, Blocked isocyanate (alkylphenol blocked isocyanate, NCO(%) = 3.2%) 8.0wt%, second iron of dimethyl dithiocarbamic acid 1.0wt% was processed like the example 1, and the constituent was prepared. Using the obtained constituent, various kinds of performance tests were performed and the result was shown in a table 1.

[0045] As well as the electrodeposited painted surface, the adhesive property over the second coat painted surface and the finishing painted surface was excellent, spreading workability is good, and is equipped with outstanding rust-proofing nature and endurance, and the obtained constituent has checked that it was very suitable as an under coat used for **** of an automobile etc. as an object for rust proofing so that clearly from the test result of a table 1.

[0046] Surface-preparation calcium-carbonate 16.7wt%, calcium oxide 2.0wt%, blocked isocyanate (alkylphenol blocked isocyanate, NCO(%) = 3.2%) 8.0wt% was processed like the example 1, and the constituent was prepared phthalic ester 33.3wt% example of comparison 1 vinyl-chloride-vinyl-acetate-copolymer (degree-of-polymerization 1900, 8.0% of vinyl acetate contents) 40wt%. Using the obtained constituent, various kinds of performance tests were performed and the result was shown in a table 1.

[0047] Although the obtained constituent had spreading workability and good storage stability and the adhesive property over the electrodeposited painted surface was also good so that clearly from the test result of a table 1, it has checked that the adhesive property over the second coat painted surface and the finishing painted surface was very poor.

[0048] Blocked isocyanate (alkylphenol blocked isocyanate, NCO(%) = 3.2%) 4.0wt%, epoxy resin (bisphenol A type weight per epoxy equivalent: 950) 3.8wt%, latency curing agent (dicyandiamide) 0.2wt% was processed like the example 1, and the constituent was prepared calcium oxide 2.0wt% surface-preparation calcium-carbonate 16.7wt% phthalic ester 33.3wt% example of comparison 2 vinyl-chloride-vinyl-acetate-copolymer (degree-of-polymerization 1900, 8.0% of vinyl acetate contents) 40wt%. Using the obtained constituent, various kinds of performance tests were performed and the result was shown in a table 1.

[0049] Although the obtained constituent had spreading workability and good storage stability and the adhesive property over the electrodeposited painted surface was also good so that clearly from the test result of a table 1, it has checked that the adhesive property over the second coat painted surface and the finishing painted surface was very poor.

[0050] Calcium oxide 2.0wt%, epoxy resin (bisphenol A type weight per epoxy equivalent: 950) 7.5wt%, latency curing agent (dicyandiamide) 0.5wt% was processed like the example 1, and the constituent was prepared surface treatment calcium-carbonate 16.7wt% phthalic ester 33.3wt% example of comparison 3 vinyl-chloride-vinyl-acetate-copolymer (degree-of-polymerization 1900, 8.0% of vinyl acetate contents) 40wt%. Using the obtained constituent, various kinds of performance

tests were performed and the result was shown in a table 1.

[0051] Although the obtained constituent had spreading workability and good storage stability and the adhesive property over the electrodeposited painted surface was also good so that clearly from the test result of a table 1, it has checked that the adhesive property over the second coat painted surface and the finishing painted surface was very poor.

[0052] Calcium oxide 2.0wt%, blocked isocyanate (alkylphenol blocked isocyanate, NCO(%) =3.2%) 8.0wt%, zinc-dimethyldithiocarbamate 1.0wt% was processed like the example 1, and the constituent was prepared surface-preparation calcium-carbonate 15.7wt% phthalic ester 33.3wt% example of comparison 4 vinyl-chloride-vinyl-acetate-copolymer (degree-of-polymerization 1900, 8.0% of vinyl acetate contents) 40wt%. Using the obtained constituent, various kinds of performance tests were performed and the result was shown in a table 1.

[0053] Although the obtained constituent had spreading workability and good storage stability and the adhesive property over the electrodeposited painted surface and the second coat painted surface was also good so that clearly from the test result of a table 1, it has checked that the adhesive property over the finishing painted surface was very poor.

[0054] Calcium oxide 2.0wt%, blocked isocyanate (alkylphenol blocked isocyanate, NCO(%) =3.2%) 8.0wt%, dimethyl dithiocarbamic acid copper 1.0wt% was processed like the example 1, and the constituent was prepared surface-preparation calcium-carbonate 15.7wt% phthalic ester 33.3wt% example of comparison 5 vinyl-chloride-vinyl-acetate-copolymer (degree-of-polymerization 1900, 8.0% of vinyl acetate contents) 40wt%. Using the obtained constituent, various kinds of performance tests were performed and the result was shown in a table 1.

[0055] Although the obtained constituent had spreading workability and good storage stability and the adhesive property over the electrodeposited painted surface and the second coat painted surface was also good so that clearly from the test result of a table 1, it has checked that the adhesive property over the finishing painted surface was very poor.

[0056] Calcium oxide 2.0wt%, blocked isocyanate (alkylphenol blocked isocyanate, NCO(%) =3.2%) 8.5wt%, dibutyltin acetate 0.5wt% was processed like the example 1, and the constituent was prepared surface-preparation calcium-carbonate 15.7wt% phthalic ester 33.3wt% example of comparison 6 vinyl-chloride-vinyl-acetate-copolymer (degree-of-polymerization 1900, 8.0% of vinyl acetate contents) 40wt%. Using the obtained constituent, various kinds of performance tests were performed and the result was shown in a table 1.

[0057] Although the obtained constituent had spreading workability and good storage stability and the adhesive property over the electrodeposited painted surface and the second coat painted surface (140 degree-Cx 10 minutes) was also good so that clearly from the test result of a table 1, it has checked that the adhesive property over the second coat painted surface (130 degree-Cx 10 minutes) and the finishing painted surface was very poor.

[0058] Calcium oxide 2.0wt%, blocked isocyanate (ketoxime blocked isocyanate, NCO(%) =4.8%) 7.0wt%, BORIAMIDO resin (amine ** 400) 2.0wt% was processed like the example 1, and the constituent was prepared surface-preparation calcium-carbonate 15.7wt% phthalic ester 33.3wt% example of comparison 7 vinyl-chloride-vinyl-acetate-copolymer (degree-of-polymerization 1900, 8.0% of vinyl acetate contents) 40wt%. Using the obtained constituent, various kinds of performance tests were performed and the result was shown in a table 1.

[0059] Although the obtained constituent had spreading workability and good storage stability and the adhesive property over the electrodeposited painted surface and the second coat painted surface was also good so that clearly from the test result of a table 1, it has checked that the adhesive property over the finishing painted surface was very poor.

[0060]

[A table 1]

	実 施 例			比 較 例						
	1	2	3	1	2	3	4	5	6	7
作業性	○	△	○	○	△	×	○	○	○	△
貯蔵安定性	○	○	○	○	○	△	○	○	○	○
伸び率 (%)	270	250	250	270	250	230	270	270	270	200
引張強さ (kg/cm ²)	35	37	35	35	37	40	35	35	35	40
接着性 (130℃×10 分)										
電着塗板	○	○	○	○	○	○	○	○	○	○
中塗塗板	○	○	○	×	×	×	△	△	×	○
上塗塗板 (ソリッド)	○	○	○	×	×	×	×	×	×	×
上塗塗板 (メリック)	○	○	○	×	×	×	×	×	×	×
接着性 (140℃×10 分)										
電着塗板	○	○	○	○	○	○	○	○	○	○
中塗塗板	○	○	○	△	△	△	○	○	○	○
上塗塗板 (ソリッド)	○	○	○	×	×	×	×	×	×	×
上塗塗板 (メリック)	○	○	○	×	×	×	×	×	×	×

[0061] Various kinds of test methods in a table 1 were based on the following all directions method specified to JASO-M -306-88 (Society of Automotive Engineers of Japan, March 30, Showa 63 amendment, automobile specification, undershirt body coating).

[0062] Workability: 5-6, storage stability:5-2, elongation-percentage:5-7, tensile strength:5-7, adhesive:5-23.

[0063] adhesive assessment -- O: -- dramatically -- fitness, **:fitness, and x: -- bad -- it comes out.

[Translation done.]